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Hydrogen bond interactions in the blends of 1,4-dioxane with some 1, 2- disubstituted ethanes at T = (298.15, 308.15 and 318.15) K

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ABSTRACT

Densities (ρ), viscosities (η), ultrasonic speeds (u) and refractive indices (n_D) of the binary blends of 1,4-dioxane (DO) with ethylenediamine (EDA), 1,2-dichloroethane (DCE) and monoethanolamine (MEA) were measured at T = (298.15–318.15) K under atmospheric pressure over the entire composition range. Various experimental data were utilized to estimate the excess molar volumes (V_m^E), excess viscosities (η^E), excess molar refractions (R_m^E), excess isentropic compressibility (κ_S^E), excess intermolecular free length (L_f^E), *etc.*, and analyzed in terms of molecular interactions and structural effects. Partial molar volumes ($\overline{V}_{m,1}{}^{0}$ and $\overline{V}_{m,2}{}^{0}$) and excess partial molar volumes ($\overline{V}_{m,1}{}^{0,E}$ and $\overline{V}_{m,2}{}^{0,E}$) at infinite dilution of the components were derived and discussed in terms of volume changes. Prigogine–Flory–Paterson theory and Peng–Robinson equation of state were used to predict V_m^E and η values of the blends. IR spectra of the blends were correlated to the molecular interactions therein the blends.

1. Introduction

Molecular interactions, operating between different liquids in liquid–liquid systems, control their physico-chemical properties and knowledge of such molecular interactions is of major significance in relation to their industrial applications [1–3] as well as in the elucidation of the structural properties of the molecules [4] in the liquid state. Mixed solvents have been used for studying complex reactions and developing theoretical understanding of chemical separations, fluid flow and heat transfers, *etc*. The basis for any design process in chemical industries is a reliable set of chemical and physical pure component along with mixture properties. Thus the determination of density, viscosity and speed of sound, *etc* are valuable tools for exploring the liquid state [5], because of the close relation between the liquid structure and macroscopic properties. Experimental values of these properties are many-a-time not at hand and the measurements are often expensive or even difficult and thus estimation methods are of great interest. These properties are functionally dependent on temperature and the composition of the liquid–liquid systems. For example, density and ultrasonic speed of sound depend on the binding forces between the liquids and are very much sensitive to the liquid structure and composition [6]. Hence studies on the physico-chemical properties of liquid–liquid systems stand as an efficient guide for the selection of such systems regarding their practical utilization in industrial and consumer applications.

Therefore in continuation of our systematic study [7–10] on the physico-chemical properties of non-aqueous liquid blends, the present study attempts to unravel the nature of molecular interactions in the binary blends of 1,4-dioxane (DO) with ethylenediamine (EDA), 1,2-dichloroethane (DCE) and monoethanolamine (MEA) at 298.15, 308.15 and 318.15 K under ambient pressure. 1, 2-disubstituted ethanes are excellent prototype for conformational studies and it is reported that relative stability of the *gauche* and *trans* conformation of 1, 2-disubstituted ethanes depend on the substituents as well as on the dielectric constant of the medium [11]. Sreeruttun and Ramasami [12] studied the conformational behavior of 1,2-dichloroethanes in several solvents by ^{1}H NMR, IR, refractive index and theoretical studies. It was found that *gauche* conformers become preferentially stabilized in media with higher dielectric constants. Nath and Singh [13] studied the binary blends of 1,2-dichloroethane with benzene, toluene, *p*-xylene, quinoline and cyclohexane. Anyway, to the best of our knowledge reports on the physico-chemical properties of the binary blends under investigation are rare in the literature. Among the selected liquids DO is a non-polar, aprotic, non-hydrogen bonded cyclic diether and finds numerous applications in industrial processes as a solvent for saturated and unsaturated hydrocarbons [14]. The other three solvents also have industrial

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importance and consumer applications, *e.g.*, EDA is an important raw material for the production of polymers, pharmaceuticals, pesticides, herbicides and dye fixing agent, *etc*; DCE is a σ-acceptor and is used as a solvent, degreaser, *etc* [13]; MEA is used in the purification of petroleum, as a solvent in dry cleaning, as a CO_2 adsorbent and as an ingredient in paints and pharmaceuticals [15]. Thus the pure liquid components for the present study were chosen based on their varied applications.

The well-established thermodynamic approach to study liquid blends is based on the interpretation of various excess properties. Hence the experimental data (ρ,η, u and n_D) were utilized to estimate the excess molar volumes (V_m^E), excess viscosities (η^E), acoustic parameters like isentropic compressibility (κ_S), intermolecular free length (L_f), specific acoustic impedance (z_{im}), excess isentropic compressibility (κ_S^E), excess intermolecular free length (L_f^E), excess specific acoustic impedance (z_{im}^E) and excess molar refractions (R_m^E) for the binary blends. Partial molar volumes ($\overline{V}_{m,1}{}^{0}$ and $\overline{V}_{m,2}{}^{0}$) and excess partial molar volumes ($\overline{V}_{m,1}{}^{0,E}$ and $\overline{V}_{m,2}{}^{0,E}$) at infinite dilution of each component were derived from the excess molar volumes (V_m^E) of the binary blends. All these functions were discussed in terms of molecular interactions, structural effects and the nature of liquid blends. Furthermore, a quantitative estimation of different contributions (*i.e.*, interaction contribution, free volume contribution and internal pressure contribution) to the excess molar volumes (V_m^E) of the binary blends at ambient temperature and pressure was determined from PFP theory [16,17]. A comparison was made between the experimental and calculated V_m^E and η values (based on PFP [16,17] or Bloomfield–Dewan viscosity model [18] and PREOS [19]) to assess the predictive capability of these theories. Moreover, ultrasonic speeds of sound and refractive indices for all the binary blends were theoretically predicted on the basis of several empirical and semi-empirical relations. In addition, IR spectra of the blends were correlated to the molecular interactions therein the blends studied.

2. Experimental

2.1. Chemicals

All the chemicals used in this work were of Reagent/Reagent Plus grade (Sigma–Aldrich, Germany, purity >99%) were used as received from the vendor. Table 1 contains provenance and purity of the chemicals used in this work. Purity of the solvents was ascertained by GLC and also by comparing their densities and viscosities at the experimental temperatures with the literature data [20–31], whenever available, as shown in Table S1 of the Supporting information.

2.2. Measurements

The binary blends were prepared by mass in air-tight bottles with stopper inside a dry box at 298.15 K and each solution thus prepared was distributed into three recipients to perform all the measurements in triplicate with the aim of the determining possible dispersion of the results obtained. The mass measurements were made on a digital electronic analytical balance (Mettler, AG 285, Switzerland) with an uncertainty of $\pm 1 \cdot 10^{-4}$g. All solutions were prepared afresh before use. The uncertainty in mole fraction was evaluated to be ±0.0002. The densities were measured with a vibrating-tube density meter (Anton Paar, DMA 4500 M). The densitometer was calibrated at the experimental temperatures with doubly distilled and degassed water and dry air at atmospheric pressure. The temperature was automatically kept constant with an accuracy of $\pm 1 \cdot 10^{-2}$K by using the built-in Peltier technique. The stated repeatability and accuracy of the densities were $\pm 1 \cdot 10^{-5}$gcm^{-3} and $\pm 5 \cdot 10^{-5}$gcm^{-3}, respectively. However, the estimated uncertainty of the density measurements for most of the pure liquids and solutions was found to be within the range 0.01–0.1%.

The viscosity was measured by means of a suspended Canon-type Ubbelohde viscometer thoroughly cleaned, dried and calibrated at the experimental temperatures with triply distilled, degassed water and purified methanol. It was filled with experimental liquid and placed vertically in a glass sided thermostat maintained constant to ±0.01 K. After attainment of thermal equilibrium, the efflux times of flow of liquids were recorded with a digital stopwatch correct to ±0.01 s. In all determinations, an average of triplicate measurements was taken into account and adequate precautions were taken to minimize evaporation loses during the actual measurements. The estimated uncertainty in viscosity measurements was 1.5%.

Ultrasonic speeds of sound (u) were measured with an accuracy of 0.3% by using a single crystal variable-path ultrasonic interferometer (Mittal Enterprise, New Delhi, F-05) working at 2 MHz. It was calibrated with doubly distilled water and purified methanol maintained at $T = (298.15 \pm 0.01)$ K by circulating thermostated water around the jacketed cell (of 2 MHz) containing the experimental liquids with a circulating pump. The uncertainty of ultrasonic speeds measurements was around ± 0.2 m s^{-1}. Refractive indices were measured with an Abbe's refractometer. It was calibrated by measuring the refractive indices of doubly distilled water and purified methanol maintained at $T = (298.15 \pm 0.01)$ K similarly as done with the ultrasonic interferometer cell. The estimated uncertainty in the refractive indices was 0.02%. The details of the methods and measurement techniques have been described elsewhere [32,33].

Table 1
Provenance and purity of the chemicals used.

Chemicals	Source	Purification method	Mass fraction purity[e]	CAS No
DO[a]	Sigma–Aldrich, Germany	Non	>0.998	123-91-1
EDA[b]	Sigma–Aldrich, Germany	Non	>0.990	107-15-3
DCE[c]	Sigma–Aldrich, Germany	Non	>0.998	106-06-2
MEA[d]	Sigma–Aldrich, Germany	Non	>0.990	141-43-5

[a] DO = 1, 4-dioxane.
[b] EDA = 1, 2-ethylenediamine.
[c] DCE = 1, 2-dichloroethane.
[d] MEA = Monoethanolamine.
[e] Purity as prescribed by the vendor.